

CLEMSON UNIV S C DEPT OF ELECTRICAL AND COMPUTER EN--ETC F/6 11/3
ELECTRONIC GRADE SILICON NITRIDE FILMS ON BULK SILICON.(U)

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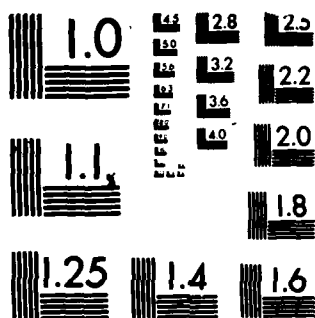
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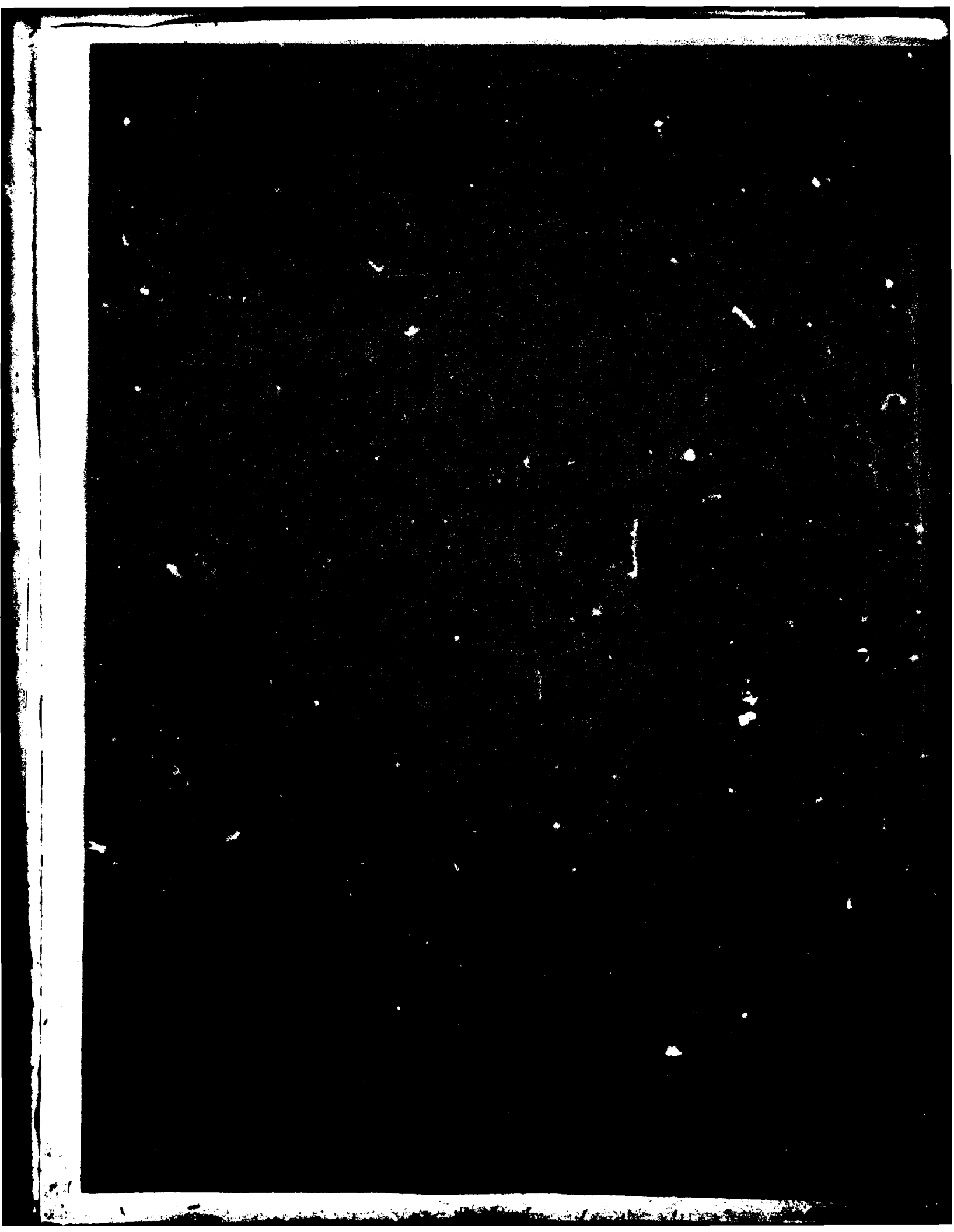
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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER RADC-TR-82-9	2. GOVT ACCESSION NO. AD-A113 252	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) ELECTRONIC GRADE SILICON NITRIDE FILMS ON BULK SILICON		5. TYPE OF REPORT & PERIOD COVERED Final Technical Report 16 Apr 79 - 31 Oct 81
		6. PERFORMING ORG. REPORT NUMBER DI-5-3591/A/M
7. AUTHOR(s) D. J. Dumin		8. CONTRACT OR GRANT NUMBER(s) F19628-79-C-0094
9. PERFORMING ORGANIZATION NAME AND ADDRESS Clemson University Dept of Electrical & Computer Engineering Clemson SC 29631		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 61102F 2306J330
11. CONTROLLING OFFICE NAME AND ADDRESS Deputy for Electronic Technology (RADC/ESR) Hanscom AFB MA 01731		12. REPORT DATE March 1982
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) Same		13. NUMBER OF PAGES 54
		15. SECURITY CLASS. (of this report) UNCLASSIFIED
		16. DECLASSIFICATION/DOWNGRADING SCHEDULE N/A
15. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) Same		
18. SUPPLEMENTARY NOTES RADC Project Engineer: Henry M. DeAngelis (ESR)		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Silicon Nitride Thin gate insulators MIS New Transistor geometries Si ₃ N ₄ Thin Films		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The production of short-channel Metal-Insulator-Semi-conductor (MIS) transistors will necessitate the use of gate insulators which can be made substantially thinner than layers of silicon dioxide can be grown. One possible insulator would be thermally grown silicon nitride. The use of silicon nitride insulators could prove to be advantageous in the development of Very Large Scale Integrated Circuits (VLSIC's) since silicon nitride offers a slightly higher dielectric constant and is a		

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better passivation layer than silicon dioxide. Transistors fabricated using thin thermally grown silicon nitride could possibly be radiation hard.

The objectives of this project were to:

- 1) design and build an open tube system capable of thermally growing silicon nitride on silicon using ammonia as the reactant gas,
- 2) study the growth parameters of the system, optimize growth conditions and produce good thermal silicon nitride films on silicon, and
- 3) fabricate simple capacitors and transistors using the silicon nitride films.

The films grown using the reactor designed at Clemson were all silicon oxide-silicon nitride multi-layer structures. These structured films are a natural product of the open tube reactor design and the system operating schedule. Reproducible thin silicon oxynitride films were grown using the reactor and all of the above objectives were met using these oxynitride films. The thickness of these films was measured as a function of growth temperature and growth time. The thinner films, in the range of 3.0 nanometers, showed substantial tunneling currents while films above 7.0 nanometers were insulators. Characterization of the films using C-V data showed that the surface state densities were of the order of 10^{11} to 10^{12} states/ev/cm² which is higher than the surface state density of high quality silicon dioxide films.

The influence of oxygen introduced during the growth cycle on film thickness is shown, and the breakdown strength and conduction mechanisms are discussed. Results of Electron Spectroscopy Chemical Analysis (ESCA) done on the films are compared for different growth processes.

The transistor characteristics showed the high gain possible with thin insulators. Transistors with P-channel mobilities in the order of 240 cm²/v sec and N-channel mobilities in the order of 350 cm² v sec were fabricated. Even using thin insulators, of the order of 5.0 nm, the yield of good transistors was very high.



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Preface

This final report prepared by Clemson University under contract no. F19628-79-C-0094, describes research primarily performed in the Department of Electrical and Computer Engineering, Dr. A. Wayne Bennett, department head.

The principal investigator was Dr. David J. Dumin. Graduate students working on the project were Mr. John Pinto and Mr. Tommy Gilstrap. In the oxidation studies we were assisted by Mr. F. Hampton of Westinghouse, Baltimore, Md. The ESCA studies were performed by Dr. James Wurzback of the Jet Propulsion Laboratories, Pasadena, Ca. Transistors were fabricated at Rockwell International, Anaheim, Ca. under the supervision of F. Erdmann and at Sandia Laboratories under the supervision of Dr. Gary Derbenwick and Dr. Paul Dressendorfer. The assistance provided by these engineers is acknowledged and is greatly appreciated.

Section I

ABSTRACT

The production of short-channel Metal-Insulator-Semi-conductor (MIS) transistors will necessitate the use of gate insulators which can be made substantially thinner than layers of silicon dioxide presently being grown. One possible insulator would be thermally grown silicon nitride. The use of silicon nitride insulators could prove to be advantageous in the development of Very Large Scale Integrated Circuits (VLSIC's) since silicon nitride offers a slightly higher dielectric constant and is a better passivation layer than silicon dioxide. Transistors fabricated using thin thermally grown silicon nitride are expected to be radiation hard.

The objectives of this project were to:

- 1) design and build an open tube system capable of thermally growing silicon nitride on silicon using ammonia as the reactant gas.
- 2) study the growth parameters of the system, optimize growth conditions and produce good thermal silicon nitride films on silicon.
- 3) fabricate simple capacitors and transistors using the silicon nitride films.

The films grown using the reactor designed at Clemson were all silicon oxide-silicon nitride multilayer structures. These structured films are a natural product of the open tube reactor design and the system operating schedule. Reproducible thin silicon oxynitride films were grown using the reactor and all of the above objectives were met using these oxynitride films. The thickness of these films was measured as a function of growth temperature and growth time. The thinner films, in the range of 3.0 nanometers, showed substantial tunneling currents while films above 7.0 nanometers were insulators. Characterization of the films using C-V data showed that the

surface state densities were of the order of 10^{11} to 10^{12} states/ev/cm² which is higher than the surface density of high quality silicon dioxide films. However, because the films were very thin, usually less than 10nm, only small shifts in flatband voltage were observed.

The influence of oxygen on film thickness is shown, and the breakdown strength and conduction mechanism are discussed. Results of Electron Spectroscopy Chemical Analyses (ESCA) done on the films are compared for different growth processes. The transistor characteristics showed the high gain possible with thin insulators. Transistors with P-channel mobilities in the order of 240 cm²/vsec and N-channel mobilities in the order of 350 cm²/vsec were fabricated. Even using thin insulators, of the order of 5.0 nm, the yield of good transistors was very high. Transistors with threshold voltages less than ±1v. were produced.

Section II

I. INTRODUCTION

Over the past two years attempts have been made at Clemson to grow silicon nitride films on silicon using ammonia as the nitriding species. The purpose of this project was to obtain thin, insulating, electronic grade silicon nitride films. The project was not entirely successful in that all of the films grown had some oxygen present. However, these films have an application in the fabrication of small transistors where the vertical dimensions would be reduced to sizes smaller than presently being used with thermal silicon oxide. If these thinner films are sufficiently thin to exhibit tunneling, they could possibly be used in the fabrication of memory transistors. The oxynitride films might also prove useful in producing radiation hard devices.

This project was prompted by work reported by T. Ito and associates at Fujitsu Laboratories in Japan (1). Ito reported growing silicon nitride films with thicknesses in the range of 10.0 nanometers. Subsequent reports concerning thermal silicon nitride films have been published (2,3,4). We have not been able to reproduce Ito's results since there was oxygen present in all of the films grown in our system.

Capacitors were fabricated on our material using mercury dots, aluminum dots and polycrystalline silicon as the contact material. Both P-channel and N-channel transistors were fabricated on our material. The properties of these devices will be described.

Section III

REACTOR DESIGN AND CONSTRUCTION

A. Chemical Reactor

Reactor

The most important piece of equipment used in the nitridation process was the chemical reactor. A schematic sketch of the reactor used can be seen in Figure 1. The high temperatures necessary for film growth were provided by a resistance heated furnace capable of reaching temperatures as high as 1200°C. Inside the furnace, a fused quartz diffusion tube provided the reaction chamber where the actual film growth took place. This diffusion tube was capable of handling silicon wafers up to two inches in diameter.

System Gas Handling

The gas handling system of the reactor was constructed entirely of stainless steel tubing. The tubing was cut and bent to create a custom installation. Upon completion of the reactor, the gas lines were pressurized to 50 psi and left for several days. The pressure remained constant, showing that the gas system was leak free.

B. Reaction Gases

Several different gases were used in the nitridation process. Each gas was regulated at the tank so that sufficient pressure was maintained. The gases were filtered to prevent particle contamination. A flowmeter was used to measure the flow rate of each gas to insure that experiments could be precisely duplicated.

A medical grade of nitrogen was employed as a carrier gas. The medical grade of nitrogen was chosen because it has a very low oxygen and water vapor content. To insure that the nitrogen was as water vapor free as possible, a

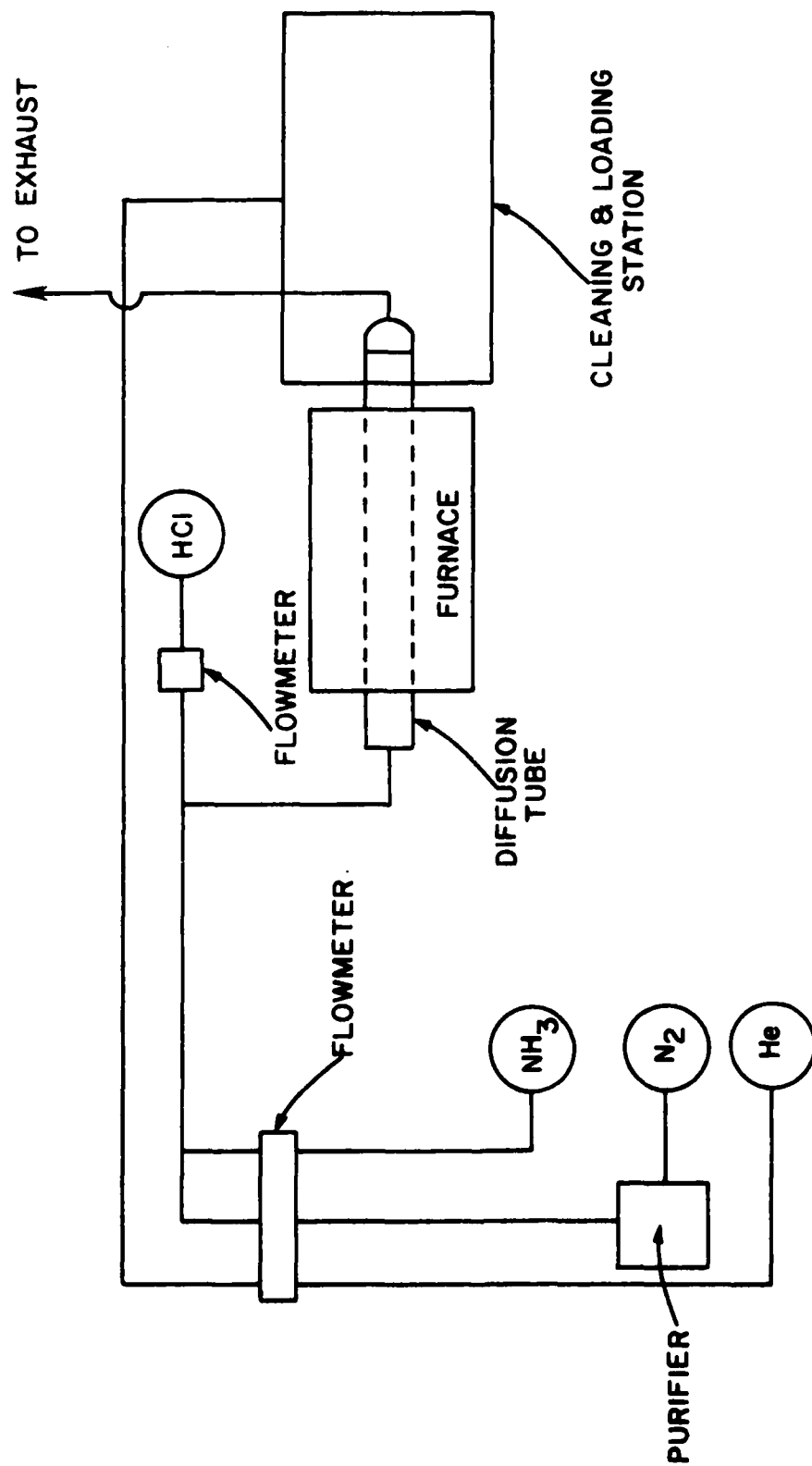


FIGURE 1. SCHEMATIC DIAGRAM OF CHEMICAL REACTOR

gas purifier was installed between the nitrogen supply and the flowmeter. The purifier used in this system was a molecular sieve manufactured by U. S. Dynamics. As designed and guaranteed by the manufacturer, this device dries nitrogen to less than one part per million (ppm) of water vapor. A constant flow of nitrogen was maintained while the furnace was in operation to minimize oxygen back-diffusion into the furnace tube. Nitrogen was also left flowing through the growth chamber when the system was not in operation.

The nitriding species was ammonia. A high purity electronic grade ammonia was chosen to minimize the oxygen and water vapor content. According to manufacturer specifications, the oxygen and water vapor content of the ammonia was less than one ppm. Both Scientific Gas Products, Inc. and Matheson Gas Co. supplied ammonia. No differences in gas supplies were observed.

An electronic grade of hydrogen chloride was used primarily as a system purge. The HCL was also used in several attempts to etch wafers inside the hot furnace.

Helium was used to limit oxygen contamination by providing an inert atmosphere where wafers could be cleaned and loaded into the diffusion tube. Clean wafers were also blown dry with helium prior to being loaded into the diffusion tube. The design of the load station called for a plexiglass hood with an open bottom where the cleaning and loading cycles would take place. A gas which was lighter than both air and nitrogen was needed to provide the inert atmosphere inside the hood. Helium was chosen because it met this requirement and was available from local suppliers.

Our initial growth experiments using the system described above yielded reproducible films of about 5.0 to 15.0 nm. Since these film thicknesses were close to those described by Ito (1) we felt that our system was properly designed and was being operated correctly. Subsequent analysis of the films

showed that they contained a high oxygen concentration. The high oxygen concentration was traced to oxygen back diffusion into the growth chamber during wafer loading. A modified load station was then designed and built.

C. Load Station Modification

In an attempt to reduce the amount of oxygen back-diffusing into the diffusion tube, the load station and loading process were modified. As seen in Figure 2, the load station was modified by first suspending a white elephant high inside the plexiglas hood. A white elephant is a wafer carrier made of fused quartz. Suspending the white elephant inside the plexiglas hood insured that the wafers, once inside the white elephant, would be in an almost oxygen free atmosphere. To further prevent oxygen from infiltrating the white elephant, a helium inlet was placed inside the white elephant so that helium would constantly flow over the wafers during the loading cycle. A second helium inlet and a baffle were placed directly under the mouth of the diffusion tube to help keep oxygen away from the diffusion tube during loading. Films grown using the modified load station were always thinner than films grown under similar growth conditions using the original load station. The nitrogen content was also higher in films grown with the modified load station. The films, however, still contained some oxygen. The amount of oxygen present in films grown using the modified load station could be varied somewhat by raising or lowering the He flow into the baffle or by changing the N₂ flow in the growth chamber during wafer loading. In general, lowering H_e or N₂ gas flow raised the oxygen concentration in the films.

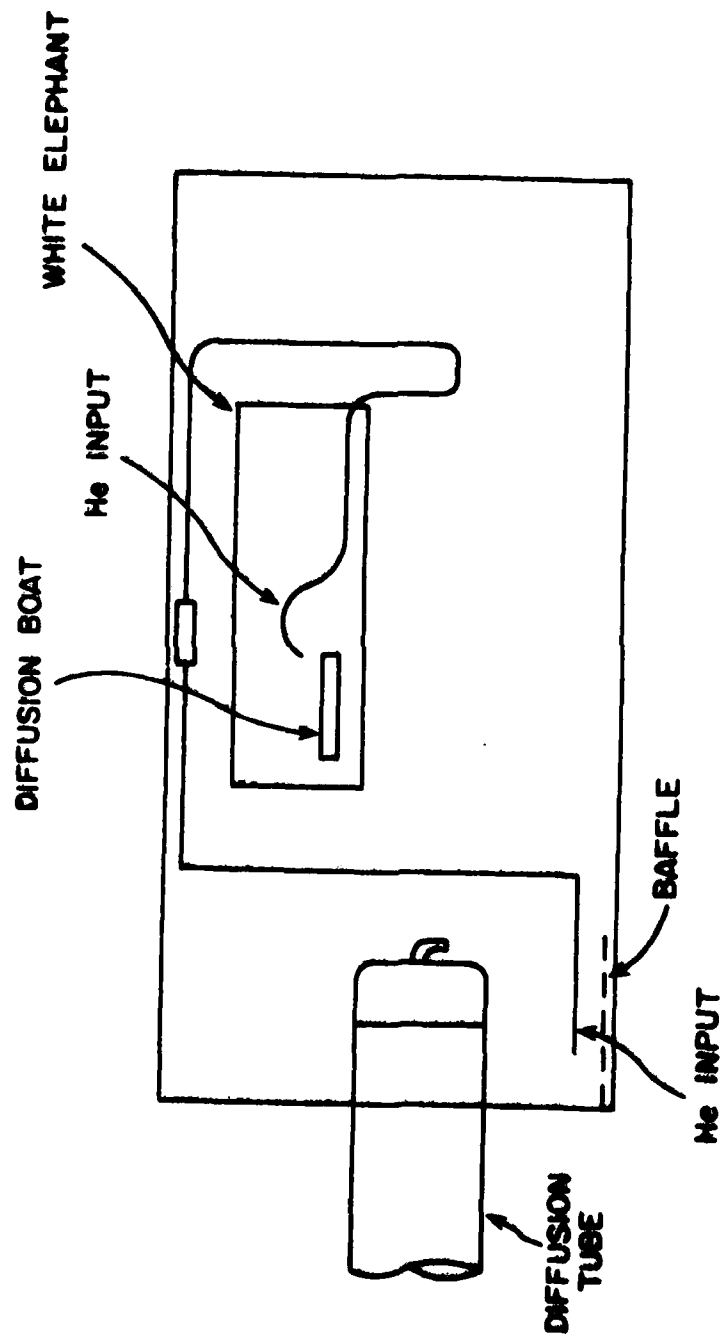


FIGURE 2. SCHEMATIC DIAGRAM OF MODIFIED LOAD STATION

Section IV

Growth of Films

The wafers used for these experiments were 2" diameter (100) or (111) silicon wafers. Both P and N-type wafers of various resistivities were used.

A. Cleaning Process

Before any nitridation was attempted, each wafer was thoroughly cleaned. First, the wafer was cleaned for 20 minutes in a 1:1 solution of hydrogen peroxide and sulfuric acid. The wafer was then rinsed in deionized water. Next, the wafer was boiled for five minutes in a 4:1:1 solution of deionized water, hydrogen peroxide, and hydrochloric acid. The wafer was rinsed a second time in deionized water. Finally, after a four minute bath in a 10:1 solution of deionized water and hydrofluoric acid and a third rinse, the wafers were blown dry with helium and loaded into the diffusion tube. After a three to five minute stabilization period, the wafer was pushed into the hot zone of the furnace. The HF bath and all rinses were performed under the plexiglas hood. The cleaned wafer never left the helium atmosphere until the growth process was completed.

B. Growth Process

Many different combinations of growth time, temperature, and flow rates were tried in order to find an optimum set of growth conditions. During the search for the optimum process, several difficulties were encountered. Methods were employed to either eliminate these difficulties or reduce their effects. For example, a growth process was attempted where the white elephant was used as a diffusion tube end cap. The white elephant fits on the open end of the diffusion tube so that a quartz sled holding silicon wafers can be slid

into the diffusion tube. A hole in the white elephant provides an access for a push rod which is used to manipulate the sled. When the white elephant was used as an end cap for an entire growth cycle, oxygen would back-diffuse through the push rod hole in the white elephant and cause the films to grow substantially thicker.

Another problem was encountered when the helium supply was low. As the helium was consumed, any water vapor in the helium tended to accumulate at the bottom of the helium supply tank. When the helium supply was nearly expended, the water vapor would be discharged either into the hood or onto the wafer being blown dry.

A most severe problem occurred when HCl gas was used in attempts to etch the wafers while in the furnace. Wafers were loaded into the furnace in a nitrogen atmosphere. The wafers were left in the hot zone of the furnace in a nitrogen flow for 20 minutes to allow any oxygen that had back diffused into the system to grow an oxide on the wafer. After the 20 minutes elapsed, HCl gas was mixed with the nitrogen at a ratio of 100:1, nitrogen to HCl. Several HCl etches were tried, from one minute to 5 minutes. Each etch damaged the wafer surface to some extent. In one run, after the HCl etch, the HCl flow was terminated and the system was purged with nitrogen for one hour. Ammonia was then allowed into the system in an attempt to nitridate the etched wafer. The wafer surface became severely pitted. The ammonia was believed to have combined with HCl residue in the furnace and formed ammonium chloride. This by-product of the etch and nitridation would severely damage the wafer. In some places the wafer had etch pits more than half way through its thickness. The same type of problem was encountered by Ito in his experiments (1).

A process which gave reproducible films was finally found. This process was to push the wafers into an open ended diffusion tube heated to the growth

temperature under a high flow rate of nitrogen while, at the same time, a high flowrate of helium flowed into the plexiglas hood. After loading the wafer into the furnace, the tube was capped, the nitrogen flow was terminated and a moderate flow rate of ammonia was introduced into the system. Growth times between two and six hours yielded reproducible results. The films grown using this process had similar electrical properties to those grown at Fujitsu Laboratories in Japan (1), but a subsequent Electron Spectroscopy Chemical Analysis (ESCA) revealed that the ratio of nitrogen to oxygen was very low. Typical N:O ratios of 1:5 to 1:8 were observed depending on the growth time. After analysis the chemical composition of the films showed that they were oxygen rich, the modified load station was designed, built, and installed. The loading process was also modified to reduce the amount of oxygen backflow. The cleaning process was unchanged, but after the wafers were cleaned and dried, they were immediately placed into the white elephant under the helium inlet. After loading the wafers in the white elephant, the end cap was removed from the diffusion tube and replaced with the white elephant. At this point the diffusion boat was pushed inside the tube and the wafers were allowed to stabilize for three minutes with a high rate of nitrogen flowing into the diffusion tube while high rate of helium was flowing into the white elephant. After the stabilization period, the wafers were pushed into the hot zone of the furnace and the white elephant was replaced with the end cap. Extreme care was taken while mounting the white elephant on the diffusion tube and when replacing the end cap so that a minimum amount of oxygen could back-diffuse into the diffusion tube. After the wafers were placed in the hot-zone, the nitrogen flow was stopped and ammonia was turned on for the desired growth time. At the end of the growth cycle, the ammonia flow was stopped and the nitrogen flow was resumed. The diffusion tube was purged with nitrogen for several minutes before the white elephant was reinstalled. The wafers were pulled back to the mouth of the diffusion tube and allowed to

stabilize for three minutes. The wafers were transferred to the white elephant and the white elephant was replaced with the end cap. Once again, the white elephant was suspended inside the plexiglas hood and the wafers were allowed to cool in the helium flow. The growth process was now completed and the wafers were ready to be characterized.

Section V

FILM CHARACTERIZATION

A. Thickness Measurement

Methods and Equipment

After a film was grown, the thickness of the film was measured by two methods. The first method used to measure film thickness was ellipsometry, and the second method was to calculate the thickness using capacitance-voltage (C-V) data. C-V analysis was also used to determine surface state density.

Ellipsometry

The ellipsometer used was the Ellipsometer II manufactured by Applied Materials. The manufacturer's specifications claimed that the ellipsometer was capable of measuring film thickness to within ± 1.0 nanometer. The device employs a helium-neon laser as the incident light source. The laser beam first passed through a polarizing lens which converted the beam to plane polarized light, then through a compensating lens which elliptically polarized the light. The film that was being measured and the wafer beneath it composed a multiple reflecting surface. As the elliptically polarized light reflected off the multiple reflecting surface, the amplitude of the light was reduced and the phase was shifted. The reflection also converted the light back to plane polarized light. The reflected light next passed through a second polarizing lens which was used as an analyzer to determine the amount of reflection. The light which passed through the second polarizing lens was picked up by a detector, and the relative intensity was displayed on a meter. The polarizing and compensating lenses were all movable. The degree of movement of the polarizer (first polarizing lens) and the analyzer (second polarizing lens) necessary to achieve a minima of reflected light was recorded. The polarizer and analyzer were adjusted and a second minima was found. The new polarizer and analyzer values were recorded. A schematic diagram of the equipment can be seen in Figure 3. The polarizer and analyzer values were

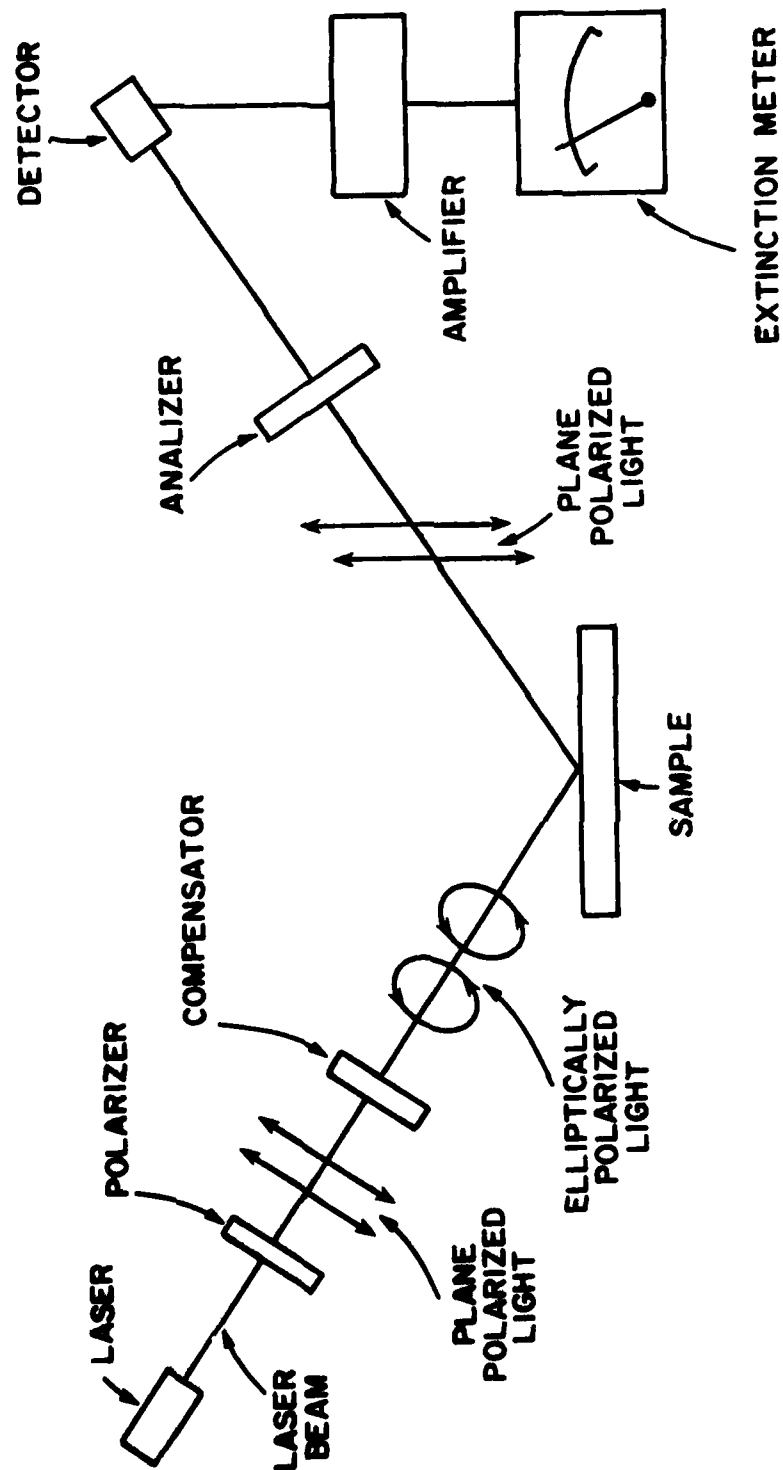


FIGURE 3. SCHEMATIC DIAGRAM OF ELLIPSOMETER

combined as shown below to give values for ψ and Δ (5).

$$\psi = ((180^\circ - A_2)/2), \text{ and}$$

$$\Delta = (P_1 + P_2).$$

In the above equations, ψ represents the arctangent of the ratio of the magnitude of the reflection coefficient for light polarized in the plane of incidence to light polarized normal to the plane of incidence and Δ represents the absolute phase shift of the same two components (6,7). The first and second analyzer readings are represented by A_1 and A_2 while the first and second polarizer readings are represented by P_1 and P_2 .

Part of the equipment included with the ellipsometer includes a nomogram, or computer generated chart, where a film's thickness and index of refraction can be obtained by simply looking up the calculated values for ψ and Δ on the nomogram. The nomogram cannot be used for extremely thin films since the thickness and refractive index lines converge. A copy of a nomogram (5) can be found in Appendix A. For the cases where the nomogram cannot be used, a table of values of ψ and Δ and the corresponding film thicknesses was also provided. The table was generated by the same computer program as the nomogram. The table lists film thicknesses in increments of 2.0 nanometers and the corresponding ellipsometer readings. To use the table, the film's index of refraction must be known or estimated. A copy of the table used to determine the film thicknesses can be found in Appendix B. A sample calculation of a film thickness using analyzer and polarizer readings from the ellipsometer can be found in Appendix C. The values for the index of refraction for our films can range from 1.45 for a pure silicon oxide film to 2.00 for a pure silicon nitride film. If the estimated index of refraction is not correct, the worst case error would give only a 0.7 nanometer error in the calculation of film thickness. In other words, a 3.3 nanometer film with an index of refraction of 1.45 will give a calculated thickness of 4.0 nanometers when the index of refraction is estimated to be 2.00. The index of refraction for films grown for this project was estimated to be 2.00.

C-V Analyses

The second method of determining the film thickness was to calculate the film thickness from C-V data. Most of the C-V measurements were taken using a mercury probe. A limited amount of C-V data was taken using either aluminum dots or polycrystalline silicon pads for the top contact. A model Hg-1C mercury probe manufactured by MSI Inc. was used to contact the wafer being analyzed. The wafer rested on a chuck on the mercury probe. The film surface was contacted by a dot of mercury while a probe contacted the back side of the wafer. The dynamic capacitance at 1 MHz was measured using a Boonton Model 71A capacitance meter. A bias voltage was applied across the film through the capacitance meter. An X-Y recorder was used to plot the capacitance versus the bias voltage. The maximum observed capacitance was the film capacitance. The film thickness was calculated from the equation (8)

$$C_1 = K_1 \epsilon_0 A / t_1$$

where C_1 is the maximum capacitance, K_1 is the estimated dielectric constant for the film, ϵ_0 is the permittivity of free space, t_1 is the thickness of the film in centimeters and A is the area of the mercury dot which contacts the wafer. The block diagram of the equipment used to take the C-V data can be seen in Figure 4. Sample C-V curves can be seen in Figures 5 and 6. A sample calculation of thickness using C-V data can be found in Appendix D.

When the growth process was completed and the sample was removed from the furnace, the cooled wafer was immediately placed on the ellipsometer, and several thickness measurements were taken. After the ellipsometer measurements were taken, the back of the sample was cleaned with HF to assure that the mercury probe could make a good ohmic contact. It was necessary to leave

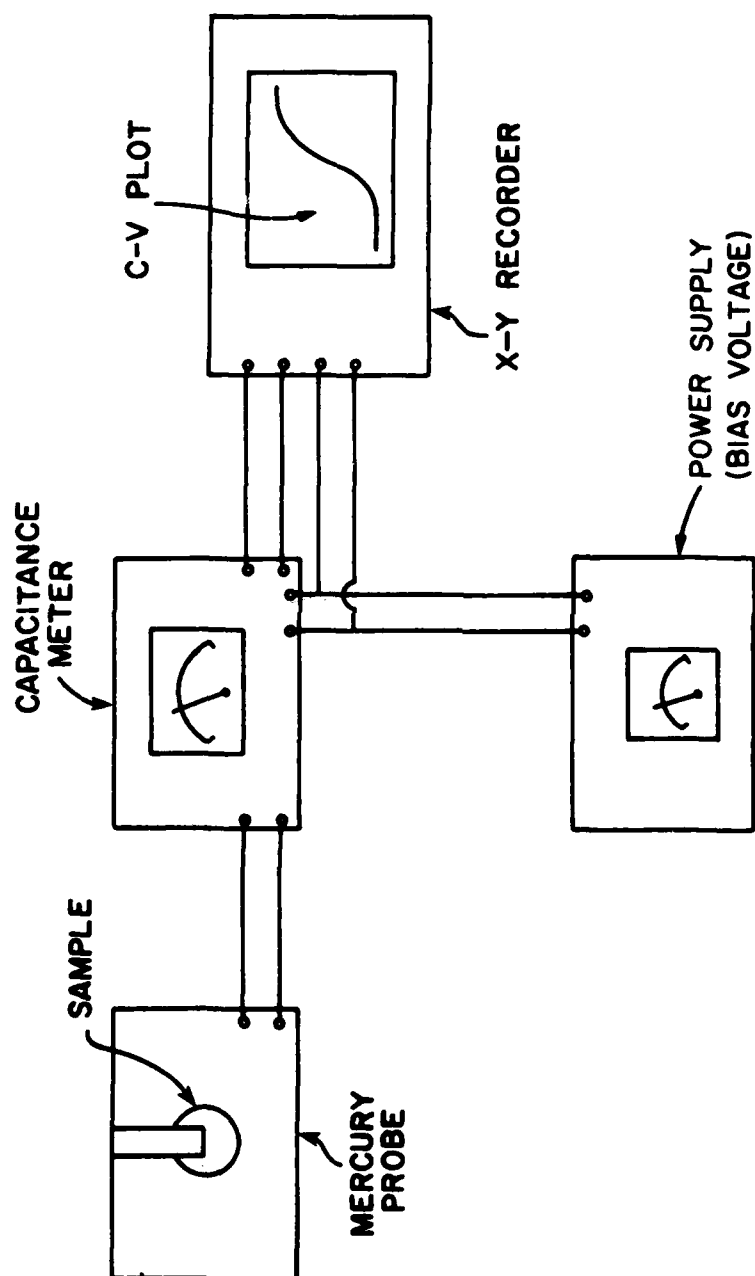


FIGURE 4. BLOCK DIAGRAM OF C-V MEASURING EQUIPMENT

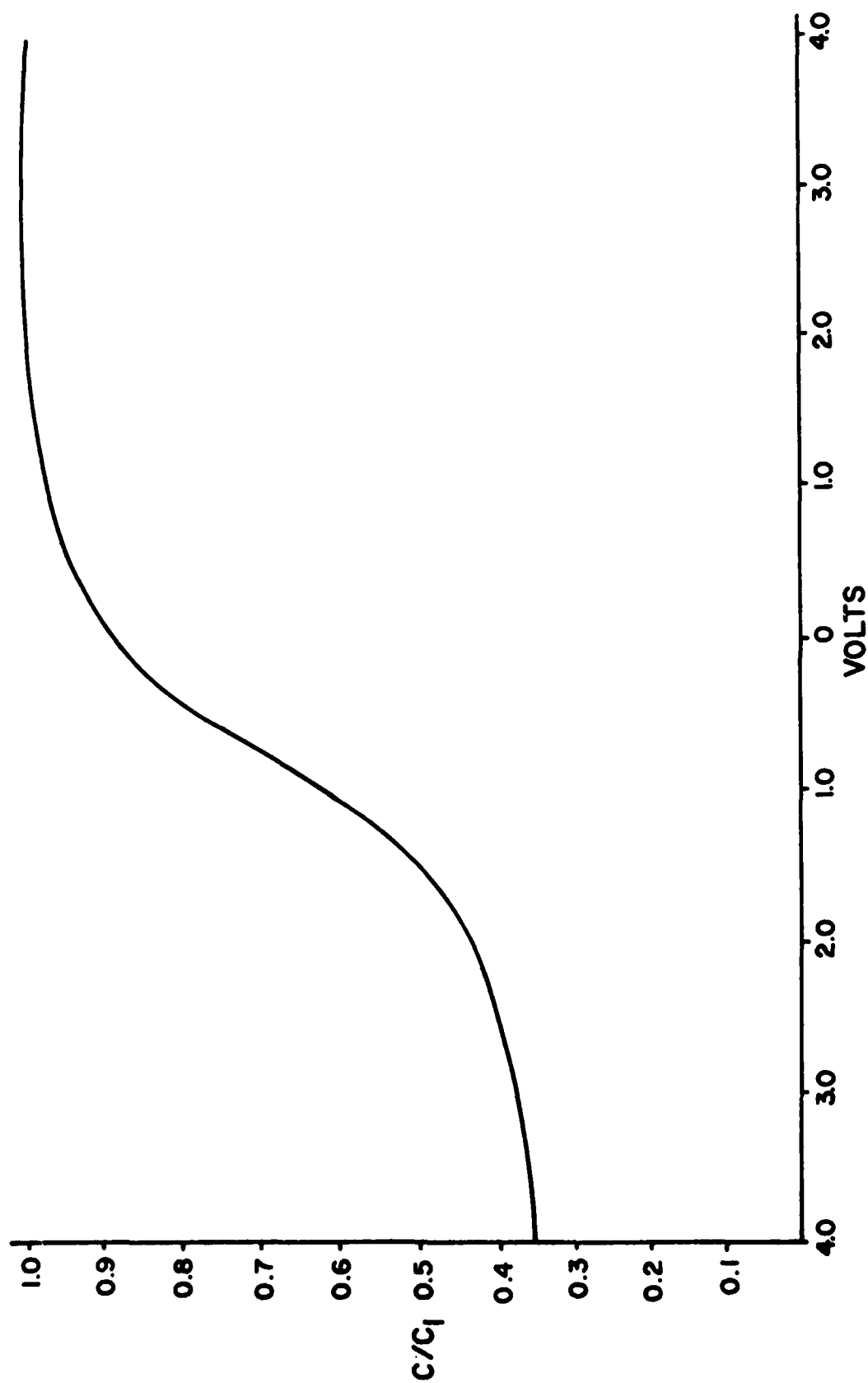


FIGURE 5 NORMALIZED C-V PLOT OF 4nm FILM ON
0.01ohm/cm, N-TYPE SILICON

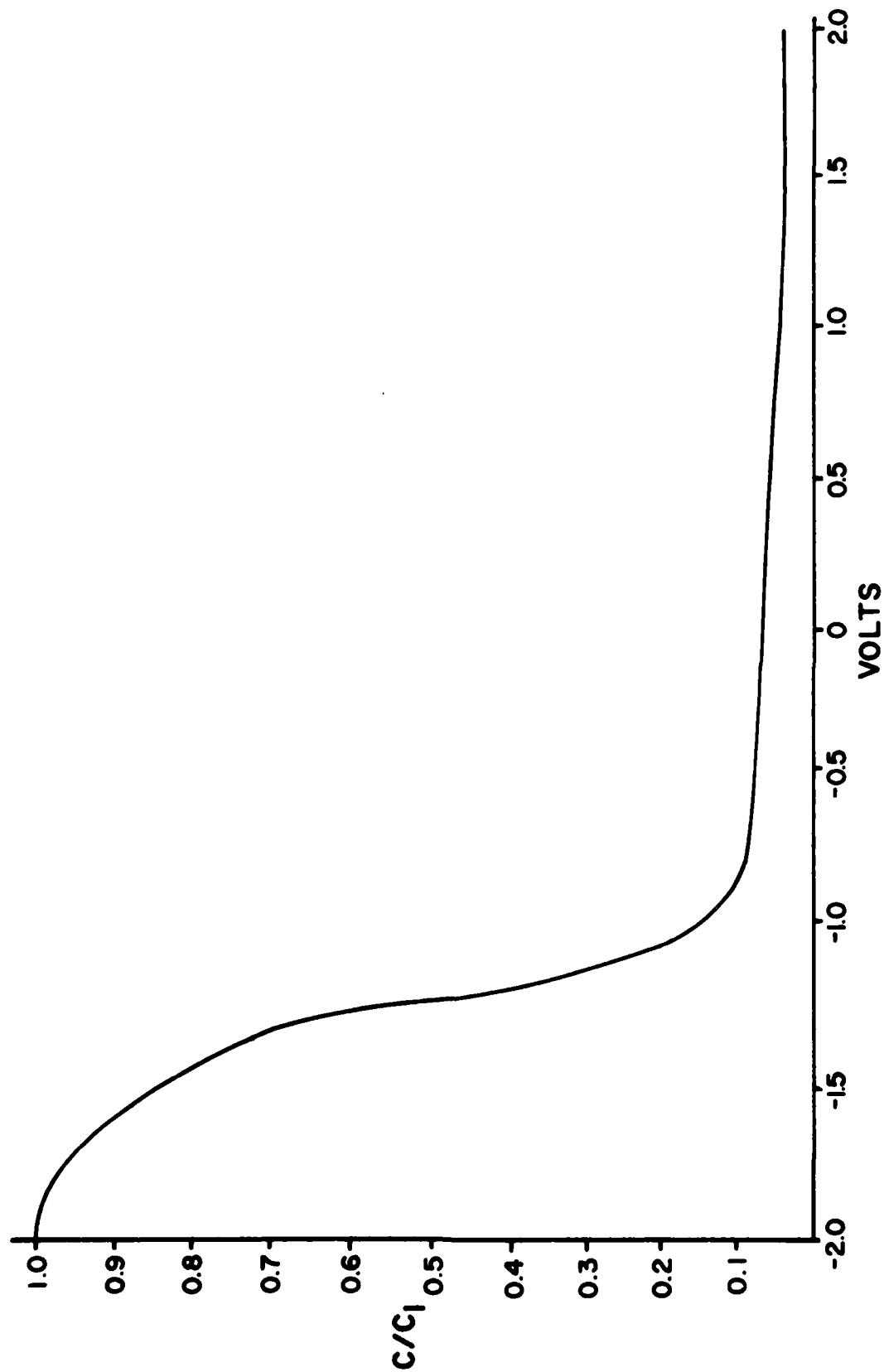


FIGURE 6. NORMALIZED C-V PLOT OF 5nm FILM ON
5 ohm/cm, P-TYPE SILICON

the HF on the wafer for a very long time, usually over five minutes, since HF etches silicon oxynitride very slowly. The etching of our silicon oxynitride films in HF is further discussed in Chapter V. When wafers with high resistivity (low dopant density) were measured, the cleaned area was coated with an eutectic of indium and gallium to aid in making the good ohmic contact. The wafer was placed on the mercury probe chuck and a C-V plot was made.

A comparison of the two methods of estimating the film thicknesses showed that the two methods were always within 1.0 nanometer and usually within 0.5 nanometers of each other.

B. Growth Rates and Analyses

When the growth process which gave reproducible results was first observed, a film thickness versus growth time and temperature study was done for 1000°C, 1100°C and 1200°C. The results of this study have been summarized in Figure 7. Each data point shown in Figure 7 represents the mean thickness of at least three different film samples. Thickness measurements taken from the center of each wafer were used to determine the mean thickness of the group of samples. The film thicknesses in this study were measured via ellipsometry. The average ellipsometer readings, ψ and Δ , for each temperature/growth time combination were compared using Hotellings T-Square with a significance level $\alpha = 0.05$. This statistical analysis revealed that, for a given growth time, the average film thicknesses obtained at any specific growth temperature were significantly different from film thicknesses obtained at other growth temperatures except those within the intervals, marked on the graph. The analysis also revealed that there is no significant increase in film thickness after four hours of growth. There was no significant difference in thickness when multiple thickness measurements from one sample were compared.

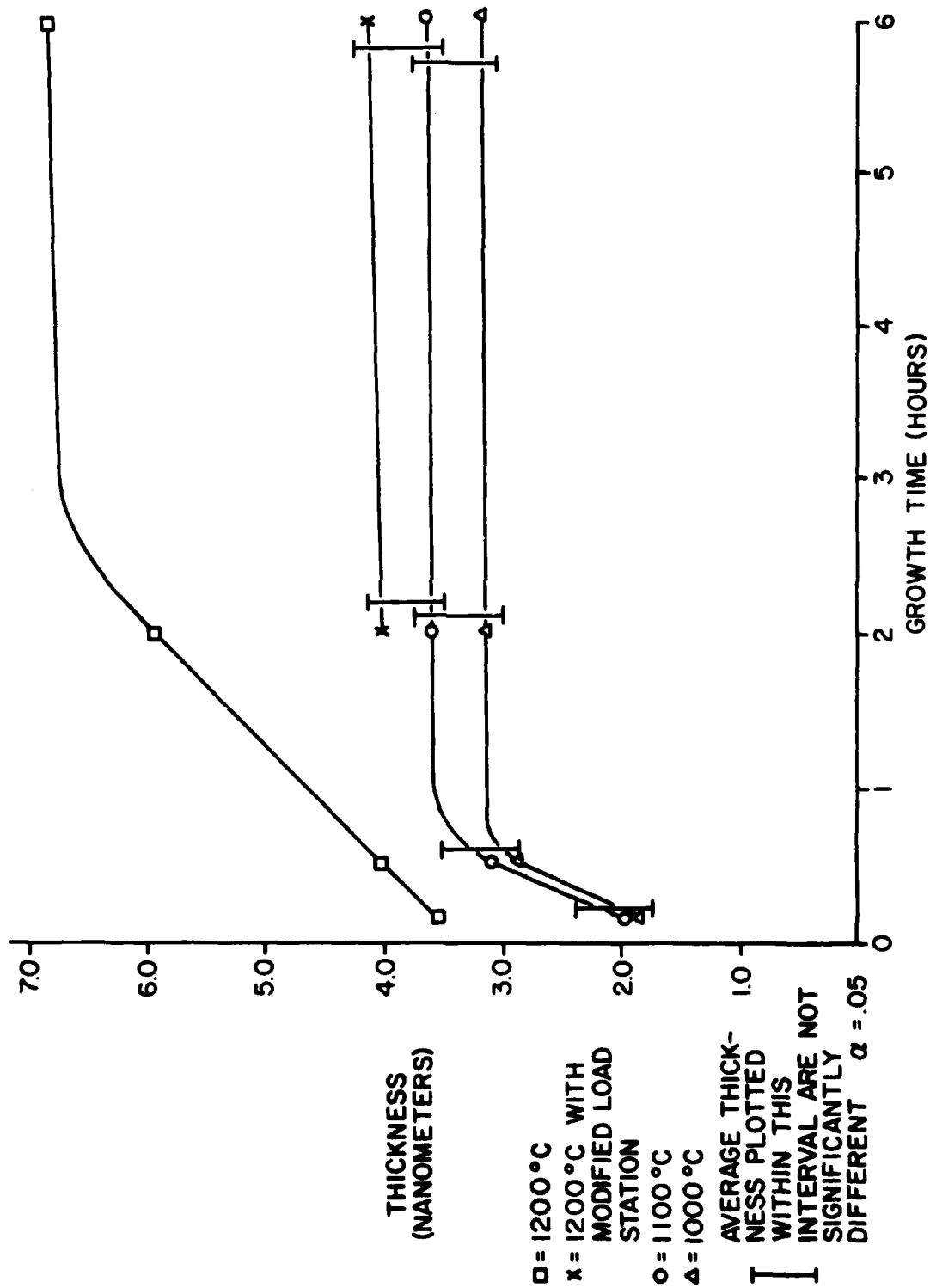


FIGURE 7. PLOT OF FILM THICKNESS VERSUS GROWTH TIME

To determine the exact nature of the films and evaluate the growth process, four samples were prepared and sent to the Jet Propulsion Laboratories to have ESCA's done on them. The preparation of each sample and the results of the analysis can be seen in Table I.

Table I. Results of First ESCA Profile

<u>Sample Number</u>	<u>Preparation</u>	<u>Results</u>
1	Cleaned only	Less than 0.5 nanometers of silicon oxide
2	Cleaned and pushed into hot zone then removed (1200°C)-no ammonia	2.0 nanometers of silicon oxide
3	Two hours growth (1200°C)	6.0 nanometers of insulator 1:8 nitride to oxide ratio
4	Six hours growth (1200°C)	7.0 nanometers of insulator 1:6 nitride to oxide ratio

Since later modification of the loading station dramatically affected the film thickness, a conclusion was made that most of the oxygen which caused the oxide to grow on Sample 2 resulted from oxygen back-diffusing into the diffusion tube during the loading cycle. This conclusion was supported by the fact that the nitrogen concentration increased with growth time and film thickness. Experiments where oxygen was purposely allowed to continually back-diffuse into the system during the growth cycle resulted in films an order of magnitude or more thicker.

The results of the ESCA analysis led to the redesign and modification of the loading station and loading process. The load station was modified as previously described in an attempt to reduce the amount of oxygen which back-diffused into the system during the loading cycle. Use of the modified load station had a substantial effect on the films grown. A film thickness versus growth time and growth temperature study was done at 1200°C using the modified load station (see Figure 7). The films grown using the modified load station had a thickness which self limited at approximately 4.0 nanometers after six hours.

Extending the growth period to 16 hours yielded a 4.5 nanometer film. A subsequent ESCA analysis on the modified load station films showed a nitrogen to oxygen ratio of 2:1.

Films grown using the modified load station showed a faster growth rate than the films grown by Ito (1,2), but the films limited at approximately the same thickness as Ito's films (1,2). Both the growth rate and limiting thickness obtained using the modified load station were nearly equal to those reported by Murarka (4).

C. Orientation and Doping Dependence

It is well known that the thickness of silicon oxide grown on silicon is a function of substrate orientation and doping density. We grew several films at 1200°C for 6 hours on (111) and (100) silicon, both P and N-type with resistivities between 10 ohm cm and 0.004 ohm cm. No statistically significant difference in film thickness could be observed.

D. Surface State Densities

Measurements and Calculations

A very important characteristic of thin films to be used in electronics applications is the interface or surface state density. Surface states are energy levels which exist in the forbidden band gap at the interface of the insulator and semiconductor. The presence of surface states enhances the recombination rate of holes and electrons at the silicon surface (8). A change in the surface state density will produce a subsequent change in the threshold voltage and a shift in the C-V plot (8).

To determine the surface state density of the films, several sample wafers were sent to Mr. F. Erdmann of Rockwell who evaporated aluminum contacts onto the film surface. Using these aluminum contacts, Mr. Erdmann did a very accurate C-V analysis. The flatband voltage, V_{fb} , and insulator capacitance, C_i , were determined from the C-V profile. Finally, the surface state density was calculated from the equations (8,9)

$$D_s = Q_i/q \text{ and}$$

$$V_{fb} = \phi'_{ms} - Q_i/C_i.$$

In the above equations, ϕ'_{ms} is the metal to semiconductor work function for the aluminum contacts, Q_i is the calculated charge density of the films, q is the electronic charge, and D_s is the surface state density.

The surface state densities for the films with the Al dots grown in this project were in the range of 10^{11} to 10^{12} states/cm²/eV. This surface state density produced a 0.56 volt shift in the flat band voltage on one of the 5.0 nanometer film samples sent to Mr. Erdmann. Decreasing the surface state density by an order of magnitude would cause the flat band voltage shift of only 0.056 volts, while increasing the surface state density by an order of magnitude would produce a 5.6 volt shift in the flat band voltage.

In the fabrication of conventional MOS transistors, a nominal thickness for a pure oxide would be in the range of 100.0 nanometers. Assuming the same surface state density of 10^{12} states/cm²/eV, the flat band voltage would be shifted by 11.2 volts. The surface state densities of the films produced by this research project are in the same order of magnitude as the surface state densities of the films produced by Ito (1,2). Fortunately the thickness of the films meant that the high surface state density produced a low flat-band voltage shift.

It should be noted that the measurement accuracy used to determine the interface state density is not very good. The thinness of our films always resulted in very small flatband voltage shifts. Thus, the values of 10^{11} to 10^{12} states/cm²/ev should be used cautiously. It may well be that the interface state density is close to 10^{11} states/cm²/ev and we were unable to accurately determine a more exact value because of inaccuracies in film thickness determination. Regardless of the amount of interface charge actually present, C-V analysis indicated a flatband voltage shift of less than ± 0.5 v for all films measured. This small flatband voltage shift is encouraging when contemplating transistor fabrication.

Section VI

FILM COMPOSITION AND THE GROWTH MECHANISM

Two basic groups of films were produced by this research project. The groups consisted of those films grown before the load station modification and those grown after the modification. An analysis was done on each group to determine the oxygen and nitrogen content of the films. The results of the analyses are discussed below and conclusions presented concerning film composition.

A. Before Load Station Modification

Analysis

As shown in Table I, the ESCA done on the films grown prior to the load station modification revealed a large amount of oxygen present as compared to the nitrogen concentration. The highest nitrogen to oxygen ratio was 1:6. This concentration ratio occurred in films with a growth time of six hours and a thickness of approximately 7.0 nanometers. All samples with a six hour growth time had film thickness of 6.0 to 8.0 nanometers. Films with growth times of two hours had film thicknesses of approximately 6.0 nanometers. The two hour sample had a concentration ratio of 1:8 nitrogen to oxygen.

It should be noted that an ESCA usually only samples the top 2nm of a film. Thus the low nitrogen-oxygen ratio is not necessarily indicative of the film composition at any place other than on the film surface. The possibility that these films are non-uniform in composition will be discussed below. In anticipation of the results of this discussion, however, the films discussed in the preceding paragraph were probably silicon nitride rich at the silicon-film interface and silicon oxide rich at the film-air interface. A graded film with a silicon oxide rich layer at the surface would account for the compositional

data presented in Table I. An examination using a Scanning Electron Microscope (SEM) revealed that the films were as smooth as polished silicon and the film surface appeared to be free of pin holes. Had the surface been pitted or rough, gas contamination would have been suspected. The concentration of nitrogen in the films was so low that the films appeared to retain some of the properties of silicon oxide films. For example, the films were readily etched in buffered HF, or rather appeared to be readily etchable in buffered HF solutions. More detailed analysis of the use of the films as a thermal oxidation barrier indicated that a short-time HF etching of the film removed only the top SiO_2 layer and not the bottom silicon nitride layer.

B. Reevaluation of Growth Process

Since the initial growth process yielded a 2.0 nanometer oxide film by simply inserting samples in the furnace, an assumption was made that the oxygen contamination resulted from back-diffusion of oxygen during the loading cycle. This assumption was supported by the fact that the nitrogen/oxygen ratio in the films increased with growth time. The high concentration of oxygen and the assumption that the oxygen resulted from oxygen back-diffusion led to reevaluation of the growth station and growth schedule, and to modification of the loading station as shown in Figure 2. Since this modification produced the biggest single change in film thickness, the majority of effort was spent on analyzing those samples grown after the load station modification.

Film samples grown at 1200°C using the modified load station were also analyzed using the ESCA process. These ESCA's were performed by Dr. James Wurzbach of the Jet Propulsion Labs. In a personal conversation Dr. Wurzbach stated that the nitrogen to oxygen concentration ratio was 2:1. These

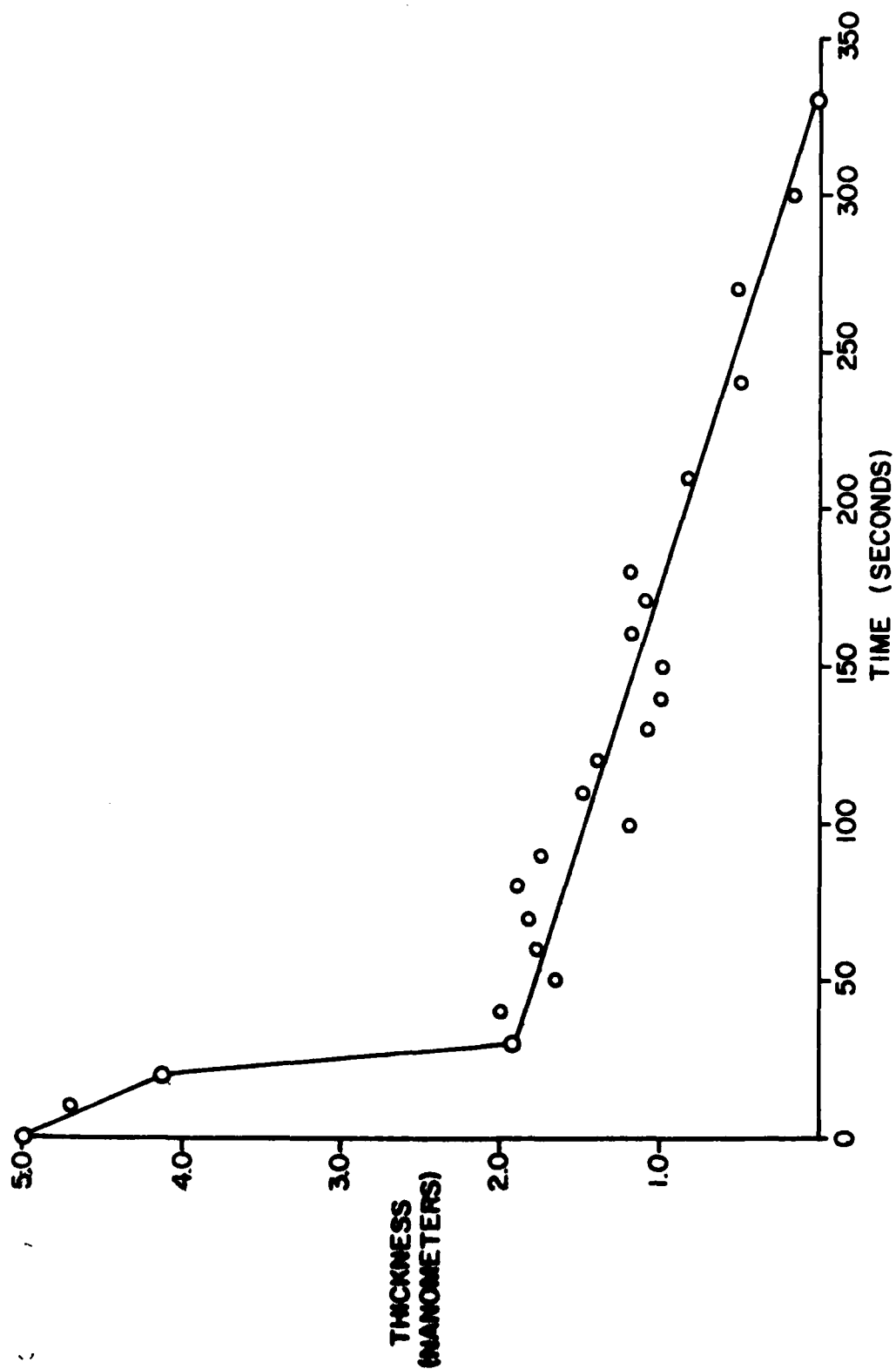


FIGURE 8. THICKNESS VS. ETCH TIME OF A TYPICAL 5.0 NANOMETER FILM

samples grew to 4.0 nanometers after two hours. The film thickness increased to only 4.5 nanometers after 16 hours. The higher nitrogen to oxygen ratio observed in these films would be consistent with the limited depth of material used for the ESCA.

C. Etch Rates and Growth Mechanism

Several of the films grown using the modified load station were etched in buffered HF. The samples were etched at ten second intervals and the thickness was measured at the end of each interval by ellipsometry.

The etch studies on a 5.0 nanometer sample suggested a film composed of multiple layers. As can be seen in Figure 8 where film thickness versus etch time has been plotted, the first layer was approximately 1.0 nanometer thick and took 20 seconds to etch. The second layer was approximately 2.0 nanometers thick and took ten seconds to etch. The third layer was approximately 2.0 nanometers thick and took 300 seconds to etch. The results of this study were very similar to the results of an etch rate study of oxynitride films done by Naiman, et al (10).

A proposed growth mechanism (see Figure 9) for these oxynitride films was developed using the etch studies and the results of Dr. Wurzbach's ESCA's. Figure 9a represents the cleaned silicon wafer as it was placed in the furnace. As oxygen back-diffused into the diffusion tube, a thin layer of oxide grew on the wafer (see Figure 9b). As the wafer remained in the ammonia atmosphere, nitrogen penetrated the silicon oxide and formed a nitrogen concentration gradient (see Figure 9c). When the nitrogen contacted the silicon oxide interface, silicon nitride began to grow at the interface (see Figure 9d) and the oxide was

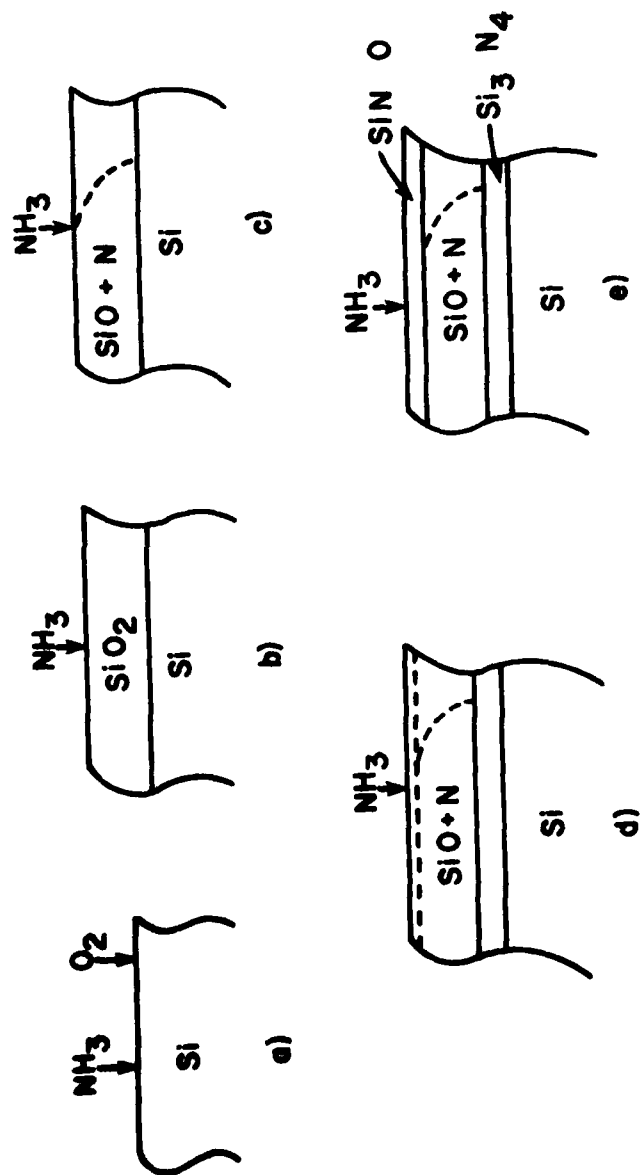


FIGURE 9. PROPOSED GROWTH MECHANISMS
FOR SILICON OXYNITRIDE FILM

pushed upward as the nitride grew. The final structure is shown in Figure 9e. Whether the nitriding species is ammonia or nitrogen cannot be inferred from the test results.

The top layer of the structure represents a nitrogen rich oxynitride which formed due to the heavy concentration of ammonia at the film surface and due to dangling surface bonds being available for chemical reaction. The second layer is silicon oxide with nitrogen of variable concentration. The third layer is silicon nitride. Variable thickness of films can be grown varying the thickness of the initial oxide layer. The etch characteristics of the silicon nitride layer is dependent on growth time and temperature, with films grown at higher temperatures and longer times being generally harder to etch.

D. Oxidation Barrier

An oxidation test was conducted to determine whether the oxynitride films would provide an oxidation barrier. Some sample wafers had wax coatings placed over half of the polished side of each wafer. The uncoated half of each wafer was etched in a 7:1 solution of H_2O and HF for two minutes. After the etching was completed, the wafers were sent to Mr. F. Hampton of Westinghouse. Mr. Hampton attempted to oxidize the wafers in various oxidizing atmospheres. An unoxidized silicon wafer was included as a monitor. Both steam and dry O_2 at $1000^\circ C$ were used as the oxidizing atmospheres. Each sample with its monitor was oxidized for one hour at a nominal temperature of $1000^\circ C$. The thickness of the film on both the etched and unetched sides of the samples was measured by ellipsometry before and after the oxidation. According to oxidation charts (8,9,11), the dry oxidation should have produced approximately 65.0 nanometers of oxide and the steam oxidation should have produced approximately 450.0

nanometers. The dry oxidation process grew 110.0 nanometers of oxide on the monitor while the steam oxidation process grew 440.0 nanometers of oxide on the monitor. The first nitrided sample grew approximately 10.0 nanometers of oxide on the etched side and approximately 1.5 nanometers on the unetched side of the wafer during the dry oxidation. The steam oxidation grew approximately 160.0 nanometers on the etched side of the wafer and approximately 90.0 nanometers on the unetched side. These results are shown in Table II.

Table II. Thermal Nitride as an Oxidation Barrier

SAMPLE 1	
Unetched Side	Etched Side
5.6 nanometers	3.7 nanometers
(After one hour of dry oxidation at 1000°C)	
7.1 nanometers	14.3 nanometers
SAMPLE 2	
Unetched Side	Etched Side
4.6 nanometers	2.4 nanometers
(After one hour of steam oxidation at 1000°C)	
93.0 nanometers	164.0 nanometers

In both the wet and dry oxidations, the unetched side of the samples grew approximately half as much additional oxide as the etched side of the sample. The dry oxidation on the unetched side of the sample produced only 6.5 percent as much oxide as produced on the clean monitor wafer. The wet oxidation on the unetched side of the sample produced only 20.7 percent as much oxide as produced on the monitor.

The oxidation test showed that neither wet nor dry oxidation was able to penetrate the unetched oxynitride to any great degree. The test also showed that the wet oxidation was able to penetrate the oxynitride film structure somewhat easier than the dry oxidation.

As shown by the results in Table 2, the initial HF etch did not remove all of film. A comparison of the results of the etch performed for the oxidation studies with the etch rate studies in Figure 8 implies that the oxidation-study films were only etched down to the nitride layer. Thus, in order to completely remove the thermally grown silicon nitride film it is necessary to etch the film for longer than 5 minutes in the HF solution. These etch studies support the growth model based on diffusion of ammonia through the silicon oxide and reaction of the ammonia at the silicon interface. These etch studies also demonstrate the relative imperviousness of the thermally grown silicon nitride films and their oxidation inhibiting properties, even at very small thicknesses.

E. Growth/Regrowth Studies

In order to corroborate the model based on growth of silicon nitride at the silicon interface covered by silicon oxide, several runs of wafers were partially or completely etched and silicon nitride regrown on the wafers. The results of one such experiment is shown in Fig. 10.

Three wafers, #67A, #67B, and #67C had a thermal nitride grown for 5.5 hours at 1200°C. The film thicknesses resulting from this growth were 5.4 to 5.6 nm as determined ellipsometrically. Wafer 67A was left unetched. Wafer 67B was etched in HF:H₂O, 1:7 for 2 min., presumably to remove the top SiN rich layer and the SiO₂ layer. Wafer 67C was etched in HF:H₂O 1:7 for 7 min. to remove all of the previously grown SiO₂ and SiN layers. The measured thicknesses after the etches were 67A = 5.5 nm, 67B = 2.6 nm and 67C = 0 nm. The wafers were all cleaned and silicon nitride was regrown on the wafer at 1200°C for 5 hours. The new thicknesses of the films were 67A = 6.7 nm, 67B = 6.8 nm and 67C = 7.5 nm. This data was interpreted to indicate that

- a) the unetched wafer effectively inhibited all but a small amount of new silicon nitride growth.
- b) the partially etched wafer partially inhibited new film growth, but was not completely impervious to new film growth.
- c) the etched wafer was as effective as a fresh substrate as far as film growth was concerned.

The variable film thickness initially and finally obtained was typically of run-to-run reproductibility. This degree of reproductibility is probably indicative of the variation in the amount of oxygen that initially back-diffused into the furnace tube during wafer loading.

A similar experiment was performed on a series of films with initial thickness of about 9-11 nm of silicon oxynitride. The thicker oxynitride was purposely obtained by allowing a small amount of oxygen to back diffuse into the

tube during initial film growth. The results of this growth/regrowth study are shown in Figure 11. The second film was purposely grown thinner than the initial film by not allowing oxygen to back diffuse into the growth tube. The results shown in Figure 11 demonstrate again the inhibiting effect of silicon nitride on regrowth of the silicon nitride film at the silicon interface.

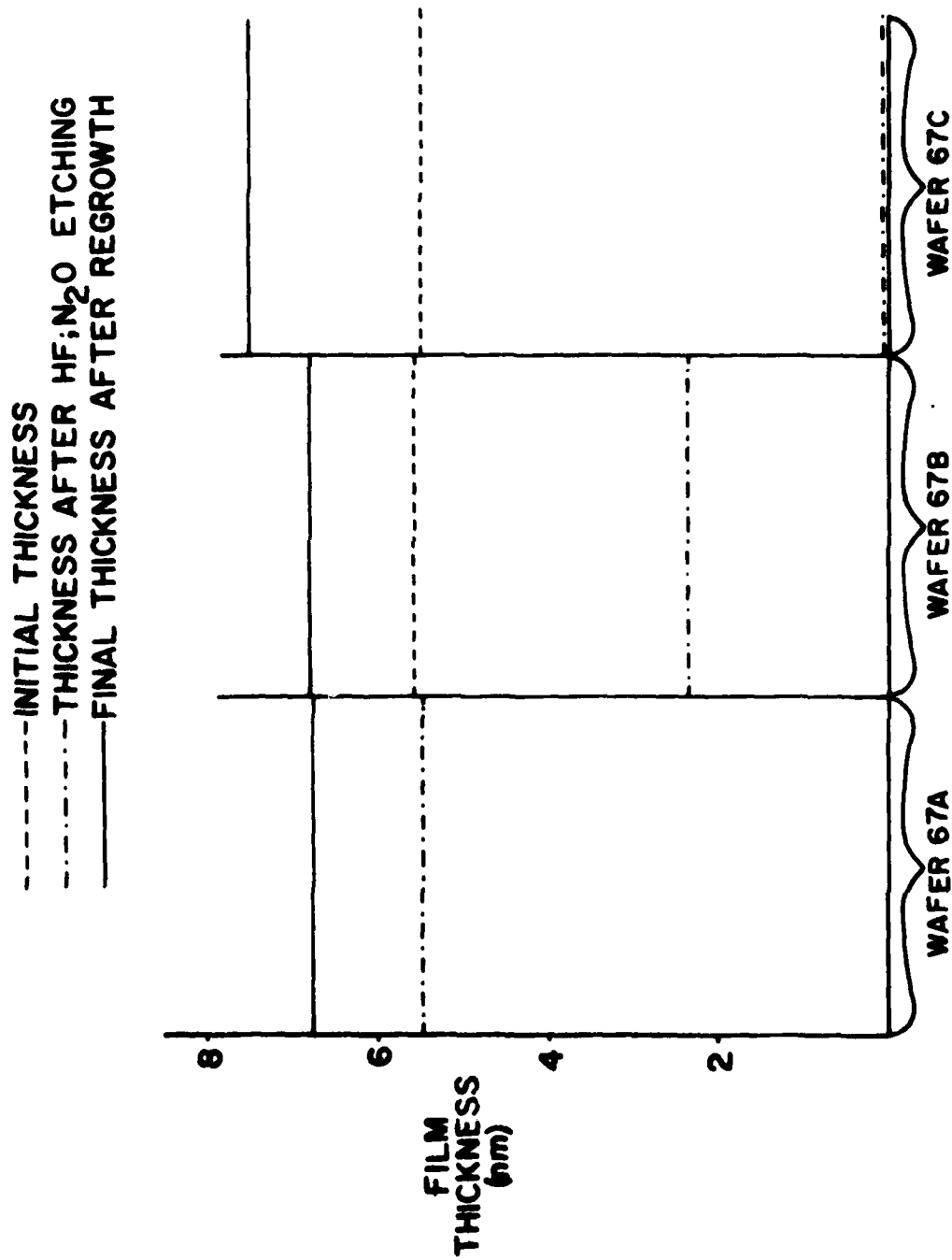


FIGURE 10. FILM THICKNESS BEFORE AND AFTER ETCH / REGROWTH OF A 5.5 nm FILM

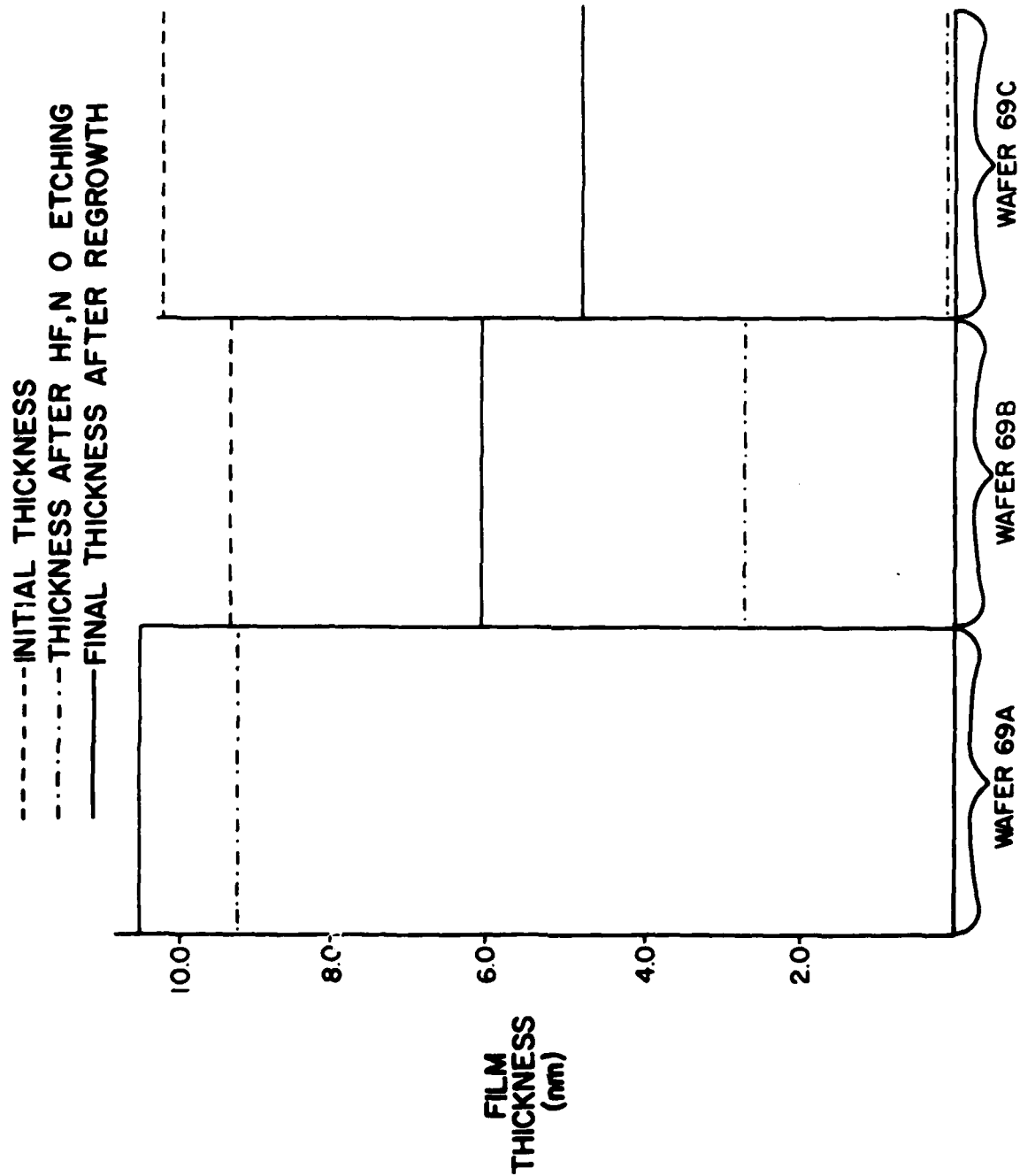


FIGURE 11. FILM THICKNESS BEFORE AND AFTER ETCH / REGROWTH OF A 9.5 nm FILM

Section VII

TUNNELING CURRENT AND CONDUCTION MECHANISM

A. Tunneling Currents

Current voltage characteristics of the films grown using the modified load station revealed breakdown voltages between 1.5 and 3 volts. Before breakdown there was nondestructive, reproducible current flow in the nanoampere range. This current was believed to be tunneling current because the I-V plot was assymetric and the plot appeared to have come from a device with tunneling in series with a Schottky barrier. Sample I-V plots are shown in Figures 12 and 13 for N-type and P-type silicon wafers.

The films grown before the modification of the load station achieved greater thicknesses for similar growth times. Those films with a thickness of 6.0 nanometers or greater were insulators. The insulating films had breakdown voltages at or above 10 volts or $8 \text{ to } 10 \times 10^6 \text{ volts/cm}^2$. The breakdown voltages were nearly equal to those reported by Sanchez-Lassise (12).

To verify the assumption that the films' conduction mechanism resulted from Schottky conduction in series with tunneling, some calculations were made using the I-V characteristics shown on Figure 12. Assuming that the forward current (8) is Fowler-Nordheim tunneling current and a rectangular potential barrier, the equation for current density is

$$J_F = C_1 \exp \frac{-4\sqrt{2m^*} (gq_b)^{3/2}}{3q\hbar E}$$

In the above equation, J_F is the current density, C_1 is a constant which includes a physical description of the barrier, m^* is the effective mass of the

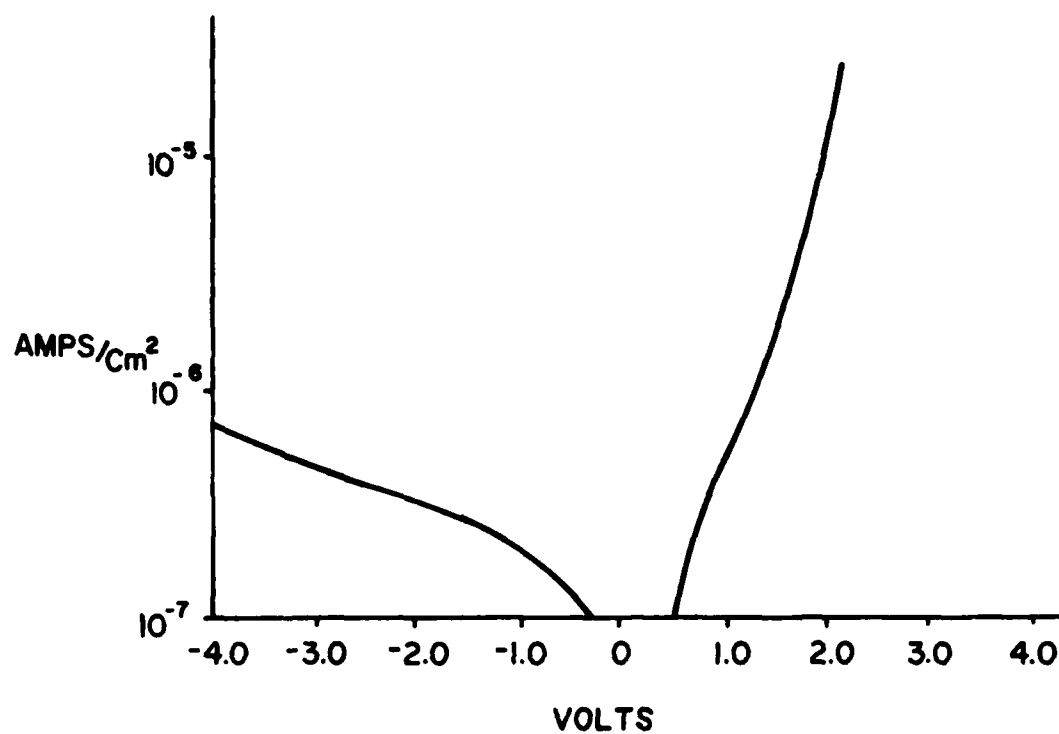


FIGURE 12. I-V CHARACTERISTIC OF FILM ON N-TYPE SILICON

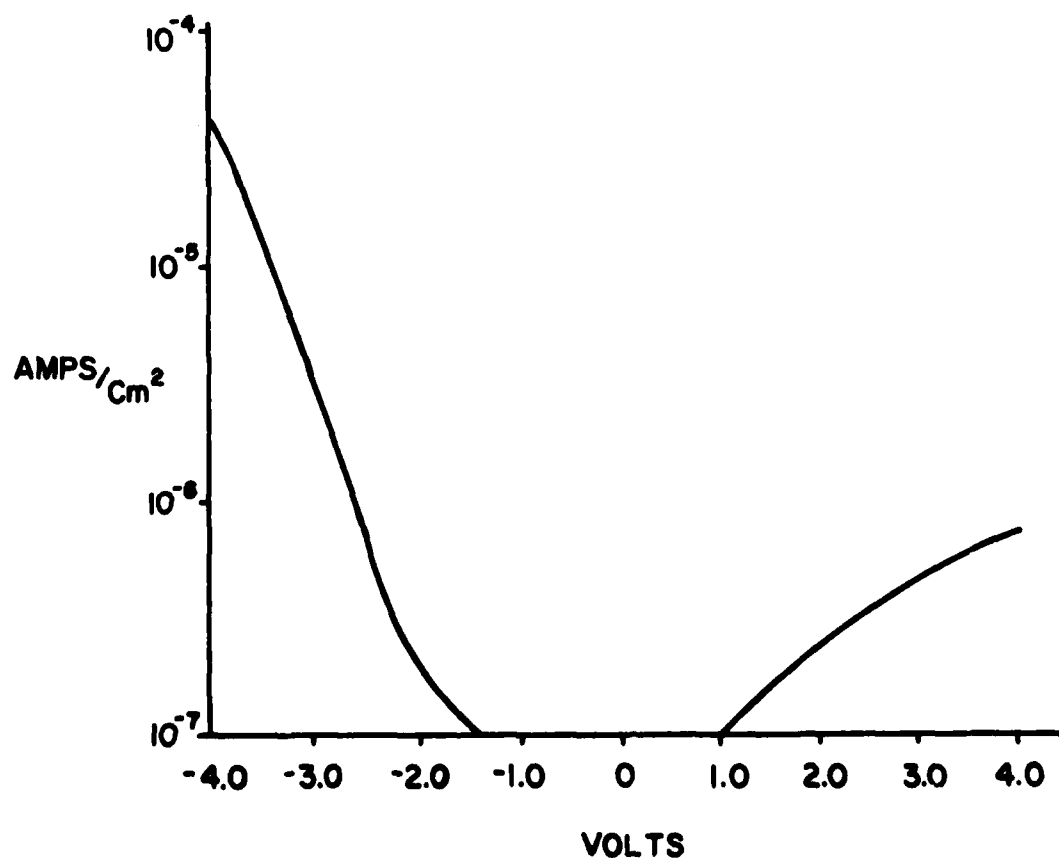


FIGURE 13. I-V CHARACTERISTIC OF FILM ON P-TYPE SILICON

charge carrier, q is the Coulombic charge, \hbar is Planck's constant divided by 2π , ϵ is the electric field, and ϕ_b is the barrier height in electron volts.

If published values (6,7) are substituted in the equation for the constants and values for J_F and ϵ are obtained from Figure 12, the barrier height, ϕ_b , is calculated to be 1.15 eV. This barrier height is comparable to published values for a 5.0 nanometer film (8).

Assuming the reverse current is a Schottky current, the equation used to calculate current is (8).

$$J_R = A^* T^2 \exp \left(-\frac{q\phi_b}{kT} \right) \exp \left(\frac{qE}{4\pi\epsilon_1} \right)^{1/2} \frac{1}{kT}$$

In this equation, J_R is the reverse current density, A^* is the Richardson constant, K is the Boltzmann constant, T is temperature in degrees Kelvin, and ϵ_1 is the permittivity of free space multiplied by the dielectric constant of the film.

If the barrier height is calculated for the reverse direction, the value is comparable to the value obtained for the forward direction. The barrier height for the reverse direction changes as the reverse voltage changes. An assumption has been made that the barrier height change is due to irregularities in the film surface. These calculations support the assumption that the conduction mechanism is tunneling current in series with Schottky current.

B. Variation of Thickness and Breakdown Voltage Across a Wafer

The I-V data and the C-V data were measured at five symmetrically placed points on a wafer. No significant variation in either I-V data or C-V data was measured. Occasionally a diode or capacitor was shorted which meant data could not be taken on this device. No attempt to quantify the incidence of short-circuited devices was made. Ellipsometer measurements did not show significant thickness variations across a wafer.

When the films were grown, three wafers were usually used in each growth run. No significant difference was ever observed in film thickness from the front of the sled to the back except in the experiment where the wafer loading end cap was left off during film growth. In that case, the film near the loading end of the furnace was much thicker than the other two, presumably due to oxygen back-diffusion during growth.

Section VIII

Transistor Studies

Attempts to make MIS transistors on silicon with thermally grown silicon oxynitride films as the gate insulator were made in conjunction with three integrated circuit manufacturers. The first attempts were only partially successful in that only a limited number of working devices were obtained.

Sandia Laboratories attempted to process a lot of 8 silicon oxynitride coated wafers into CMIS transistors. The oxynitride films ranged in thickness from 3 nm to 6 nm. None of the N-channel transistors probed were functional. Only a very small number of the P-channel transistors operated successfully. Most of the devices showed high gate leakage and a 1 to 2 volt gate offset voltage. The devices operating in the depletion transistor mode. A drain characteristic of one of these devices measured at Sandia Laboratories is shown in Figure 14. These transistors were very sensitive to gate shorts during probing. The high gate leakage current appeared to be due to tunneling of carriers through the thin gate insulator.

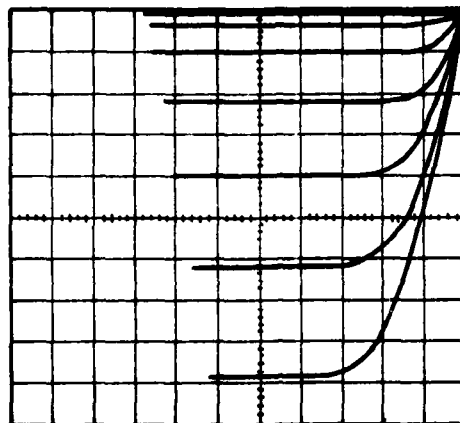
The problems encountered with these first devices were discussed with Sandia personnel and with engineers at Rockwell International. It was decided to modify the fabrication process to better account for the thinness of the insulator and for the fabrication schedule needed to produce the silicon oxynitride. The second attempt at fabrication CMIS transistors at Sandia Laboratories was more successful. Transistors with channel lengths nominally 4 μm were made on 14 films. The silicon oxynitride was systematically varied from 3 nm to 14 nm. Both P- and N-channel devices were made. All wafers had working devices and transistor characterization is continuing. Both P-channel and N-channel device characteristics are shown on Fig. 15 and Fig. 16. Assuming length/width ratios of 30 for the N-channel transistors and 90 for the P-channel transistors, field effect mobilities of 350 cm^2/vsec and 240 cm^2/vsec were obtained for the N-channel and P-channel transistors, respectively.

Engineers at Rockwell International used 8 wafers of silicon oxynitride on silicon to produce P-channel MIS transistors. The 6 wafers that were processed to completion all had working transistors. The circuit used by RI is shown in Figure 17. The drain characteristic of a typical RI fabricated transistor is shown in Figure 18. Complete characterization of these wafers is continuing. Attempts will be made to test radiation hardness of these transistors.

No quantitative measure of transistor yield is available at this time. However, it is relatively unusual to find a non-working device on either the Sandia or the Rockwell International wafers. The incidence of gate shorts does appear to rise on the devices made using silicon oxynitride films less than 6 nm, however.

An interesting characteristic of both P-channel and N-channel devices has been observed. The transistor gain appears to drop about 40% and the threshold voltage appears to rise about 0.5 to 1.0 v as the device is operated on a curve tracer. This effect is reversible by reversing gate voltage polarity. Whether this effect is due to contamination of the gate insulator or due to electron trapping within the insulator is not yet known.

A2145A/4 $V_{T_p} \sim -1.3 \text{ V}$
 OFFSET = -1.3 V 8 STEPS



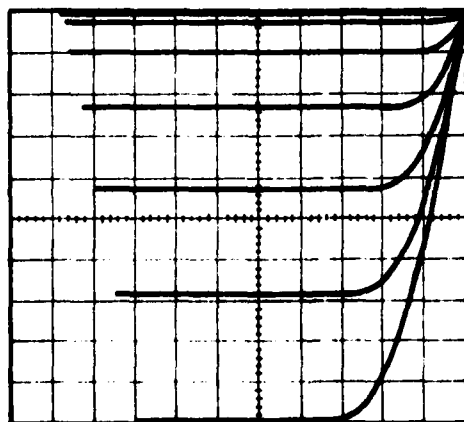
100 μA
 PER VERT DIV

 200 mV
 PER HORIZ DIV

 100 mV
 PER STEP

 1 m
 g_m PER DIV

A2145A/4 $V_{T_p} \sim -1.3 \text{ V}$
 OFFSET = -1.3 V 7 STEPS



100 μA
 PER VERT DIV

 200 mV
 PER HORIZ DIV

 100 mV
 PER STEP

 1 m
 g_m PER DIV

FIGURE 14. DRAIN CHARACTERISTIC OF EARLY
 P-CHANNEL TRANSISTOR FABRICATED AT SANDIA
 LABORATORIES

2145A-18

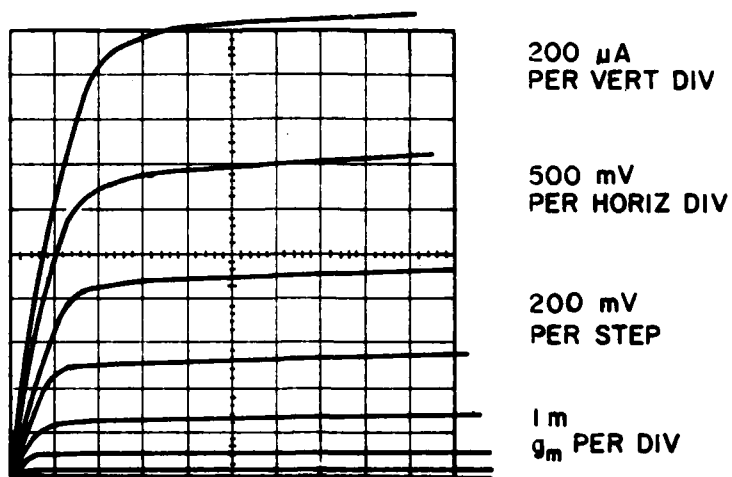


FIGURE 15. N-CHANNEL DRAIN CHARACTERISTIC OF
DEVICE FABRICATED AT SANDIA LABORATORIES

2145A-18

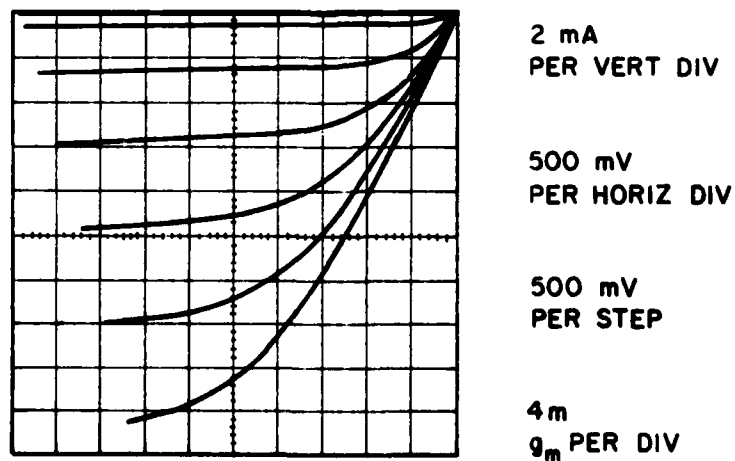


FIGURE 16. P-CHANNEL DRAIN CHARACTERISTIC OF
DEVICE FABRICATED AT SANDIA LABORATORIES

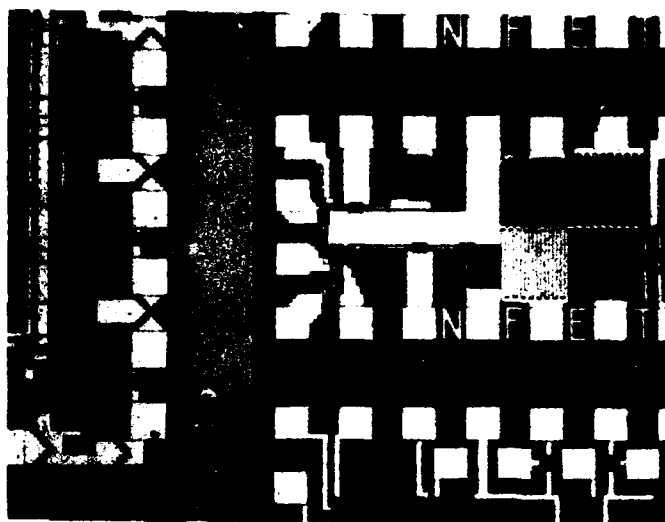


FIGURE 17. MICROPHOTOGRAPH OF ROCKWELL INTERNATIONAL TRANSISTOR ARRAY

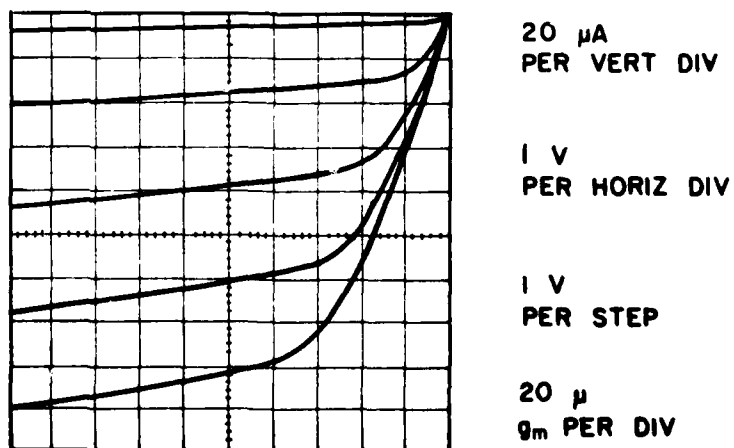


FIGURE 18. DRAIN CHARACTERISTIC OF A 2 μm LONG RI TRANSISTOR

Section IX

CONCLUSIONS

Thin insulating silicon oxynitride films have been grown in a chemical reactor. These insulating films proved to be reproducible and they were in the 4.0 to 7.0 nanometer range for long growth times at high growth temperatures. These films showed considerable resistance to an HF etch and proved to be good oxidation barriers. The thinner films showed the presence of tunneling currents. These films were oxynitrides with oxygen concentration decreasing as the back diffusion of oxygen during the growth cycle was decreased. The higher concentration of nitrogen near the silicon-insulator interface suggested a growth process based on nitrogen or ammonia diffusion through the insulator causing nitridation of the substrate. The limited film thickness obtained after long nitridation times indicated that these films become excellent diffusion barriers to nitrogen or ammonia. These films also were excellent oxidation barriers. At the present time whether the nitriding species is nitrogen or ammonia is not known.

The possibility of growing a pure nitride film using this open tube reactor system is doubtful without extensive modification of the loading station. Also, a hot wall system may inherently lead to either oxygen or water vapor contamination due to the hot quartz walls and may limit the practicality of the system with respect to obtaining pure silicon nitride. Regardless of the care taken to eliminate oxygen from the diffusion and carrier gases, a certain amount of oxygen will back-diffuse into the diffusion tube during the loading cycle.

If these films are to be used in any type of production atmosphere, precautions would have to be taken to insure that the wafers are oxide free before the growth process begins. These precautions may include modifications of present industrial cleaning and loading methods.

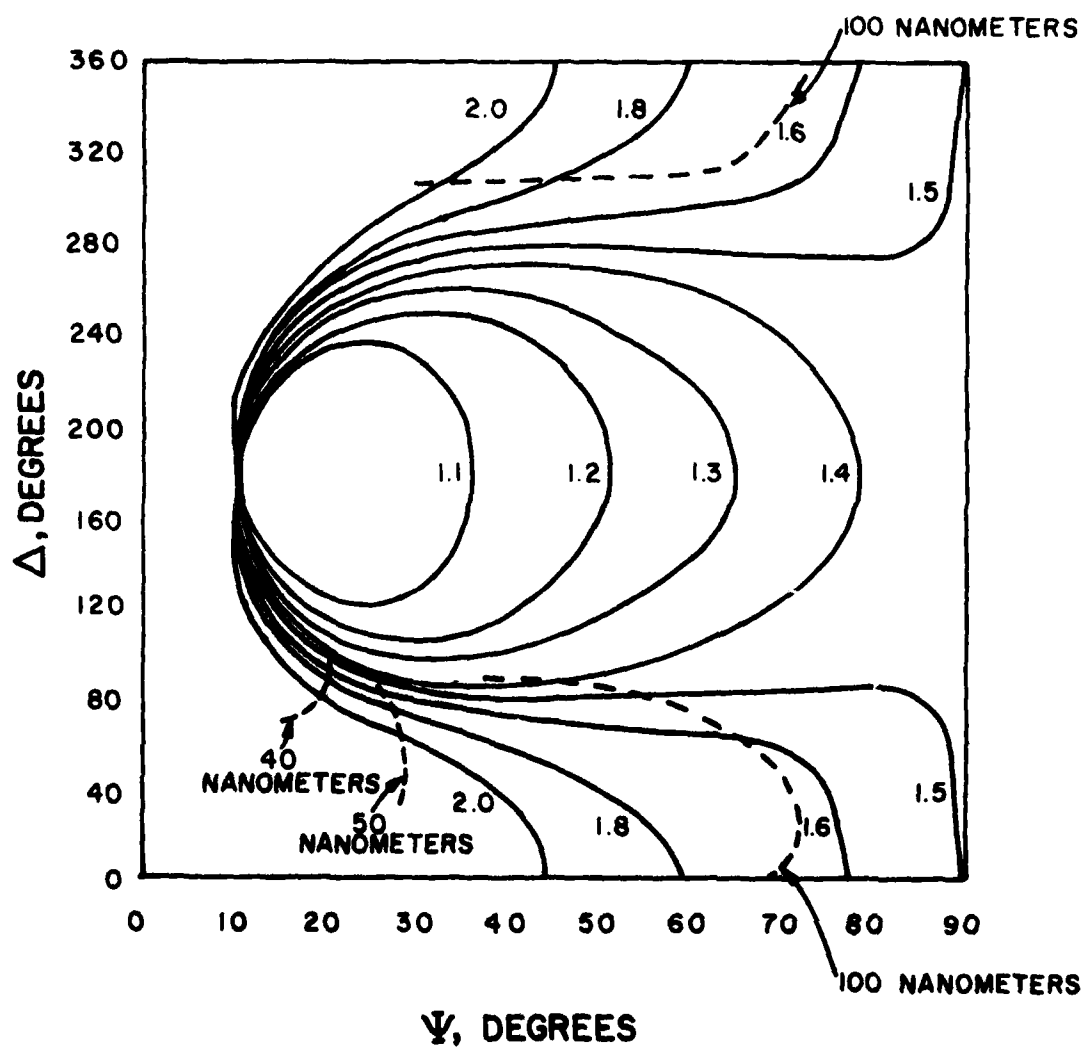
An alternative growth process suggested by M. Naimen of Lincoln Labs would be to grow a controlled thin oxide film and then nitridate the film at

relatively low temperature. The final film thickness could be controlled by the initial oxide thickness and could be in the 3.0 to 30.0 nm range.

This project has shown that it is possible to grow very thin, high quality electronic grade films which could be used in the fabrication of useful MIS devices. These films showed a high degree of resistance to HF etching. These films also are useful as oxidation barriers during device production MIS transistors have been fabricated on these films. The transistors showed reasonable characteristics for devices fabricated with thin insulators as the gate material.

APPENDICES

APPENDIX A ELLIPSOMETER NOMOGRAM



Appendix B
Thickness Chart

Refractive Index 2.00

Thickness	Delta	Psi
0	179.16	10.34
2.0	172.15	10.39
4.0	165.24	10.52
6.0	158.50	10.73
8.0	151.99	11.00
10.0	145.76	11.35
12.0	139.84	11.75
14.0	134.24	12.10
16.0	128.95	12.70

Appendix C

Ellipsometry Thickness Calculation

Assume the following ellipsometer readings:

A1	A2	P1	P2
14.20	173.35	36.20	125.67

$$\psi = ((180^\circ - A2) + A1) / 2 = 10.63$$

$$\Delta = (P1 + P2) = 161.87.$$

Using the table in Appendix B, the nearest value to the above Δ is 158.58 which represents 6.0 nanometers. This value and the one for 0 nanometers are used as follows:

$$179.16 - 158.50 = 20.66,$$

$$179.16 - 161.87 = 17.29,$$

$$17.29 / 20.66 \times 6 = 5.0 \text{ nanometers.}$$

Appendix D

Capacitance/Thickness Calculation

Assume a maximum film capacitance of 5700 pico farads. Using the following equation:

$$t_1 = K_1 \epsilon_0 A / C_1$$

K_1 = approximate film dielectric constant = 4

ϵ_0 = permittivity of free space

$$\epsilon_0 = 8.862 \times 10^{-14} \text{ F/cm}$$

$$A = \text{area} = 0.0081 \text{ cm}^2$$

C_1 = maximum film capacitance

$$C_1 = 5700 \text{ pico farads}$$

$$t_1 = 5.0 \text{ nanometers.}$$

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